



National Institute of Standards & Technology

Report of Investigation

Reference Materials 8562-8564

8562: CO₂-Heavy, Paleomarine Origin (carbon dioxide)

8563: CO₂-Light, Petrochemical Origin (carbon dioxide)

8564: CO₂-Biogenic, Modern Biomass Origin (carbon dioxide)

These Reference Materials (RMs) are intended to provide carbon dioxide samples of known isotopic composition and uncertainty with ¹³C/¹²C and ¹⁸O/¹⁶O ratios expressed in parts per thousand difference (‰) from Vienna Pee Dee belemnite (VPDB) or Vienna Standard Mean Ocean Water (VSMOW) [1]. RMs 8562-8564 are not certified, but their use allows comparability of stable carbon and oxygen isotope ratio data obtained by investigators in different laboratories. Assigned values, based upon intercomparison results and high accuracy measurements at NIST, may be used to normalize laboratory standards. A RM unit consists of two borosilicate glass tubes, each 9 mm in diameter and about 30 cm in length. Each tube contains approximately 400 μmol of gas and is labeled with a unique number that, if necessary, can be used to identify preparation variables.

RM Preparation: RMs 8562, 8563, and 8564 were prepared by R.M. Verkouteren, Surface and Microanalysis Science Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology (NIST). Details of the preparation method are published elsewhere [2]. RM 8562 was prepared in 1995 from carbon dioxide provided by T.B. Coplen, U.S. Geological Survey (USGS). This gas originated from natural thermal decomposition of a Jurassic limestone deposit in the Southeastern United States, and was sampled through a well in 1982 [3]. RM 8563 was prepared in 1996 from SFE-grade carbon dioxide (99.999 %) obtained from Scott Specialty Gases, Plumsteadville, PA. This gas originated from combustion of byproducts from a petrochemical refinery in the Eastern United States. RM 8564 was prepared in 1996 from research grade carbon dioxide (99.995 %) obtained from Scott Specialty Gases, Plumsteadville, PA. This gas originated from the fermentation of C₄ biomass (corn) in a grain distillery in the Central United States.

Storage and Use: Until use, it is recommended that these RMs be stored in their original container at ambient temperature (20 °C to 30 °C). Before use, the user's inlet system should be conditioned with carbon dioxide of isotopic composition similar to the RM. To open, the RM requires the proper use of a suitable tube cracker [4-7], and after opening should be used immediately for calibration or standardization. If desired, a sample can be stored in a clean glass breakseal or container fabricated with an all-glass stopcock coated with a hydrocarbon-based grease, or other vessel known to preserve the isotopic integrity of carbon dioxide [8].

Note: Because very limited quantities of these materials exist, distribution is limited to one unit (two tubes) of each RM per three-year period of time. Users are strongly advised to prepare their own internal standards for routine quality control and to normalize or compare those standards with these RMs.

The supporting aspects concerning distribution of these RMs were coordinated through the Standard Reference Materials Program by N.M. Trahey.

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Isotope Compositional Values: Assigned $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values and uncertainties for the RMs were determined by two complementary methods: 1) through accurate measurements of delta values *between* RMs ($\Delta\delta^{45}\text{CO}_2$, $\Delta\delta^{46}\text{CO}_2$, and $\Delta\delta^{47}\text{CO}_2$), and 2) through an international comparison exercise.

D $\delta^{45}\text{CO}_2$, D $\delta^{46}\text{CO}_2$, and D $\delta^{47}\text{CO}_2$ Values: These measurements were performed at NIST to determine accurate compositional differences between RMs. In this method, instrumental design and protocols were used where the *measured* $\delta^{47}\text{CO}_2$ value was statistically equal to the *expected* $\delta^{47}\text{CO}_2$ value (as calculated from $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$). This condition was achieved only when all three measurements were accurate, which on the NIST instrument required special ion source modifications and unusual measurement protocols [2]. While the resulting measurements defined precisely the relative compositions among the RMs, standardization onto the VPDB scale required the consensus process described below.

Intercomparison: Each of thirteen participating laboratories was requested to measure replicate RMs, apply a conventional reduction algorithm to the $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$ measurement data, and standardize the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values onto the VPDB scale through NBS19-CO₂ [1,9,10]. Most the participating laboratories also reported $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values for CO₂ derived from other standard materials, including LSVEC, NBS18, IAEA-CO-9, NBS22, VSMOW, and SLAP. By normalizing the RM values to common standard compositions [1,11], improvements were realized in reproducibility. Results are summarized in Tables 1 and 2 as ranges of reported and normalized $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$ values. The ranges in values are due to interlaboratory variations in VPDB realization and instrument calibration; the median standard deviation of replicate analyses of any RM was about 0.02 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$.

Value Assignment: With the relative differences between the three RMs characterized accurately, realization of VPDB scale was made through the intercomparison results by using the RMs having the most precise normalized values for $\delta^{13}\text{C}_{\text{VPDB}}$ and $\delta^{18}\text{O}_{\text{VPDB}}$. These were RM 8562 ($\delta^{13}\text{C}_{\text{VPDB}} = -3.76 \text{ ‰} \pm 0.03 \text{ ‰}$) and RM 8564 ($\delta^{18}\text{O}_{\text{VPDB}} = +0.19 \text{ ‰} \pm 0.10 \text{ ‰}$). Through these assignments, the values of the remaining delta values were thereby fixed with acceptable precision; these are listed in Tables 1 and 2. The combined standard uncertainty (u_c) of each assignment includes the uncertainty (standard deviation) in the defining RM, the standard deviation of the $\Delta\delta^{45}\text{CO}_2$ and $\Delta\delta^{46}\text{CO}_2$ measurements, and the known sample-to-sample isotopic variation (described in the following section) combined in quadrature. In all cases, these value assignments were within the range of results reported in the intercomparison.

Table 1. Values for $\delta^{13}\text{C}_{\text{VPDB}}$ (in ‰)

Reference Material	Range of Reported Values	Range of Normalized Values	Value Assigned and Uncertainty (u_c)
RM 8562 (CO ₂ -Heavy)	-3.81 to -3.60	-3.80 to -3.72	-3.76 (0.03)
RM 8563 (CO ₂ -Light)	-41.67 to -40.96	-41.79 to -41.26	-41.56 (0.06)
RM 8564 (CO ₂ -Biogenic)	-10.54 to -10.27	-10.54 to -10.36	-10.45 (0.04)

Table 2. Values for $\delta^{18}\text{O}_{\text{VPDB}}$ (in ‰)

Reference Material	Range of Reported Values	Range of Normalized Values	Value Assigned and Uncertainty (u_c)
RM 8562 (CO ₂ -Heavy)	-8.77 to -7.98	-8.57 to -8.25	-8.45 (0.11)
RM 8563 (CO ₂ -Light)	-24.08 to -22.97	-23.86 to -23.43	-23.72 (0.11)
RM 8564 (CO ₂ -Biogenic)	-0.23 to +0.48	+0.07 to +0.39	+0.19 (0.10)

The $\delta^{18}\text{O}_{\text{VPDB}}$ values may also be expressed versus VSMOW or VPDB-CO₂ through the following conversion formulae [1]:

$$\begin{aligned}\delta^{18}\text{O}_{\text{VSMOW}} &= (1.0309 \times \delta^{18}\text{O}_{\text{VPDB}}) + 30.9 \\ \delta^{18}\text{O}_{\text{VPDB-CO}_2} &= (\delta^{18}\text{O}_{\text{VPDB}} - 10.25) / 1.01025\end{aligned}$$

Isotopic Uniformity: After production, the RM tubes were heated to 70 °C for 24 h to accelerate potential isotopic exchange of carbon dioxide with trace water vapor and the silicate interior of the tubes, then were allowed to incubate for at least one month before each RM batch was characterized (see Table 3). Determination of the isotopic heterogeneity of each RM batch was facilitated through a uniform sampling design where samples were selected for measurement (through their unique identifier) to explore the effects of inherent nuisance factors documented during RM production – fortunately, no factors were significant. Measurements on RM 8562 and RM 8563 were performed at NIST using very high precision methods [2], while measurements on RM 8564 were performed at USGS using typical methods. No datum was excluded as a statistical outlier. Observed isotopic variability was apportioned between instrumental effects and true sample-to-sample heterogeneity.

Table 3. Isotopic Variations in CO₂ Reference Material Populations (in ‰)

Reference Material	Estimated RM variation in $\delta^{13}\text{C}$ (sample to sample heterogeneity, $\pm U$)*	Estimated RM variation in $\delta^{18}\text{O}$ (sample-to-sample heterogeneity, $\pm U$)*
RM 8562 (n = 44)	0.0073 \pm 0.0029	0.0253 \pm 0.0070
RM 8563 (n = 50)	0.0039 \pm 0.0039	0.0134 \pm 0.0037
RM 8564 (n = 43)	0.0044 \pm 0.0085	0.0183 \pm 0.0116

*Expanded uncertainties, U , are symmetric (and conservative) 95 % confidence levels [12].

Stability: RM isotopic stability was determined after one to two years of incubation by measuring twelve samples of each RM. No additional variance was observed in these sample sets as compared to the original sets used to assess isotopic heterogeneity. Differences in compositional means were significant (at the 95 % confidence level) in three cases, but these differences were small and probably due to long-term instrumental effects. The isotopic stability of these RMs will continue to be monitored until one year after stocks are exhausted. For more information, access the Website at <http://acg.nist.gov/outputs/CO2.html>.

Normalization Procedure: These RMs may be used to determine normalized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of laboratory standards (LS) through the equation below [1,13], where δ^m values are measured or assigned $\delta^{13}\text{C}$ ($m = 13$) or $\delta^{18}\text{O}$ ($m = 18$) values for two RMs (RM1 and RM2) that bracket the composition of the laboratory standard. Upon establishing the normalized composition of at least two laboratory standards, these in turn may be used to determine routinely the normalized compositions of samples. When reporting normalized delta values of samples, the assigned compositional values of the RMs should also be reported.

$$\delta_{\text{LS,normalized}}^m = \delta_{\text{RM1,assigned}}^m + \left[\frac{\delta_{\text{LS,measured}}^m - \delta_{\text{RM1,measured}}^m}{\delta_{\text{RM2,measured}}^m - \delta_{\text{RM1,measured}}^m} \right] \times \left[\delta_{\text{RM2,assigned}}^m - \delta_{\text{RM1,assigned}}^m \right]$$

Absolute Ratios: The absolute ratios of $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$, reported in relevant primary standard materials, are summarized below. The precisions of the values reported are not justified by their uncertainties, but rather by the requirement of consistency of their “accepted values” used in data reduction algorithms for high precision intercomparability of standardized $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The expanded uncertainty is defined as $U = k \times u_c$, where u_c is the combined standard uncertainty and k is a coverage factor of 2 [12].

Table 4. Absolute ^{13}C and ^{18}O Abundances in Primary Standard Materials

Primary Standard Material	$^{13}\text{C}/^{12}\text{C} \pm U$	$^{18}\text{O}/^{16}\text{O} \pm U$	References
PDB-Chicago	$(11\,237.2 \pm 60) \times 10^{-6}$	N/A	14
RM 8544 (NBS19-limestone)	$(11\,201.5 \pm 28) \times 10^{-6}$	N/A	15
RM 8535 (VSMOW)	N/A	$(2005.20 \pm 0.45) \times 10^{-6}$	16

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Users of this RM should ensure that the report of investigation in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet <http://ts.nist.gov/srm>.